

## Report 6

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## Persistence of Diquat in Three Field Environments

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### ABSTRACT

Diquat, a contact herbicide, was applied to three test locations in the Sacramento Delta area which were infested with *Egeria densa*: White Slough (WS), Owl Harbor (OH), and Sand Mound Slough (SM). The persistence of diquat in each of these locations was monitored at 1, 3, 6, 12 and 24 hours following application. Samples were taken at 1 foot below the surface and 1 foot above the bottom at each of three sites within the test plot (2,3, and 4) and two sites on either side of the test plot (1 and 5). Method EPA 549.1 was used for diquat analysis providing recoveries averaging  $88.41 \pm 8.1$  % for laboratory water and  $76.5 \pm 10.0$  % for field water (due to binding to particulates).

### INTRODUCTION

*Egeria densa* is a submersed weed which grows in fresh and brackish water environments with limited water movement. It is a hazard and nuisance to boat traffic in waterways, wrapping itself around propellers and making movement difficult. Assembly Bill 2193, passed in 1997, authorized the California Department of Boating & Waterways to control growth of *Egeria* in the Sacramento San Joaquin Delta and its tributaries. Diquat is one of a small number of herbicides which are registered for application to surface water. It has low acute toxicity and is not persistent in water. Diquat can be used in water that will be used for swimming, irrigation, and consumption by livestock or by man -- as soon as laboratory analysis shows that the water does not contain more than 10 ppb of diquat cation (1). Its suitability as a control agent for *Egeria densa* was therefore investigated.

References suggest that one of the principal means of diquat inactivation is through binding to soil or other particulates (2,3,4), which can be plentiful in Delta waterways. In addition there are few literature studies in which diquat was applied to environments that have tidal water movement. Because of this, the persistence of diquat in the test locations long enough to give *Egeria* control was of particular concern. The purposes of this study were twofold: 1) determine whether persistence in each of the three sites was sufficient to control *Egeria* 2) determine what site characteristics / tidal conditions were most closely correlated with persistence of diquat.

## MATERIALS AND METHODS

### Application and Site Description.

Three test locations were chosen within the Sacramento Delta., and within each, a test plot approximately 1 acre in area was established. Diquat was applied by airboat from hoses that injected the herbicide just below the water surface. All plots had plentiful quantities of *Egeria densa* at the time of the first application.

### Sampling

Prior to diquat application six water samples in duplicate were collected to monitor background and to serve as a basis for matrix spikes. This project was designed so that for each set of samples (a set is a group of samples drawn after the same application) there are three matrix spikes, two matrix blanks, three laboratory spikes and two laboratory blanks.

Applications were timed to take advantage of the reduced water volume associated with an extremely low tide, and took about 1- 1.5 hours for Department of Water Resources personnel to complete. Samples of the tank mix were collected during application for three of the five applications. Water samples were collected at 1, 3, 6, 12, and 24 hours after the start of spraying at five different sites in each of the test plots. The sites were arranged as shown in Figure 1 : sites 2, 3 and 4 were within the test plot, with site 4 on the opposite side of the channel from 2 and 3. Sites 1 and 5 were upstream and downstream of the test plot, respectively. For each site, the water depth was measured and duplicate samples were taken at 1 foot above the channel bottom and 1 foot below the water surface using a 12- volt bilge pump connected to a plastic hose to pump water from the desired depth.

Water samples were collected in 500 mL high density amber PVC bottles (diquat is light-sensitive) to which 12.5 mL conc.  $\text{H}_2\text{SO}_4$  was added within 30 min of collection to preserve the analyte. The bottles were capped tightly and shaken 15 to 20 times to ensure thorough mixing of acid and water. They were then packed in ice and brought to the laboratory within 3 to 6 hours of collection, and refrigerated ( $4^\circ\text{C}$ ) until extraction. Most samples were extracted within 3- 24 hours of arrival, and those that were not were extracted within 2 weeks of collection, with no noticeable loss of analyte. (samples held under refrigeration for 4 to 5 weeks suffered noticeable degradation and manpower was adjusted to prevent this)

### Diquat Analysis

Diquat was analyzed using EPA method 549.1 (5) which is based on ion pairing with hexanesulfonic acid in a C-8 solid phase extraction format.

### Solutions for Analysis:

Conditioning Solution A : Cetyltrimethylammonium bromide ( 95%, Aldrich, 0.5 g) and concentrated ammonium hydroxide ( ACS grade, 5 mL) were dissolved in 1 L of deionized water.

Conditioning Soln. B: 1-Hexanesulfonic acid sodium salt ( 98%, Aldrich, 10 g), and concentrated ammonium hydroxide (ACS grade, 10 mL) were dissolved in 500 mL deionized water.

Cartridge Eluent : Orthophosphoric acid (85%, reagent grade, 13.5 mL) and diethylamine (reagent grade, 10.3 mL) were dissolved in 1 L deionized water.

Mobile Phase : Orthophosphoric acid (85%, reagent grade, 13.5 mL), diethylamine (reagent grade, 10.3 mL) and 1-hexanesulfonic acid sodium salt (98%, Aldrich, 3.0 g) were dissolved in 1 L of deionized water.

*Laboratory Ware Preparation :* Before initial use, all glassware which would come in contact with diquat was silanized (Supelco Sylon CT, or equivalent). This precaution is necessary to prevent adsorption of diquat onto glass surfaces. Alternatively, plasticware was used. Plasticware was washed with detergent, rinsed in tap water and distilled water and was drained dry before use.

*Standard Preparation :* Diquat dibromide standard was purchased from ChemService and used to make solutions that contained 1 mg/mL of diquat cation in water. This solution was used to prepare each day's working solutions : 0.15, 0.50, 1.50, 50.00, and 150.00 ng/ul (corresponding to 3, 10, 30, 100 and to 300 ppb in the original water sample). The 150 ng/ul solution was made as follows : To a 15-mL graduated polypropylene centrifuge tube were added 4.5 mL of Cartridge Eluent, 150 ul of Ion Pair Concentrate and 75 ul of 1 mg/mL diquat stock. The volume was brought up to 5 ml with Cartridge Eluent and the tube vortexed well. The 50 ng/ul solution was made up similarly except 25 ul of 1 mg / mL standard were used. All other concentrations came from repetitive 10-fold dilutions of these.

*Sample Preparation:* Solid phase extraction cartridges (Varian Bond Elut, Cat No. 1210-2053) containing 500 mg of C8 Packing were first conditioned with the following sequence of washes at approximately 10 mL/min : deionized water (5mL), methanol (5mL), deionized water (5mL), Conditioning Solution A (5 mL), deionized water (5 mL), methanol (10 mL), deionized water ( 5 mL) and Conditioning Solution B ( 10 mL). These cartridges were either used immediately or sealed with a closed stopcock and parafilm to prevent drying and stored at 4°C for a maximum of 48 h.

Prior to analysis each sample was filtered with the aid of air pressure using a 0.45 u, 47 mm nylon filter secured in a polypropylene holder and topped with a 75 mL polypropylene reservoir. A 250 mL aliquot of the filtrate was taken and adjusted to pH 10.5 ( $\pm$  0.1) using 20% sodium hydroxide and 6 N sulfuric acid. Since diquat is unstable under basic conditions, this was immediately loaded on a conditioned C-8 cartridge with the aid of a 75 mL reservoir and passed through the cartridge under vacuum at a flow rate of 3-6 mL / min. When the last of the sample was even with the top of the sorbent bed, 5 mL of methanol were added to the top of the cartridge and passed through at the same 3-6 mL / min flow rate.. The column was then dried by passing air through it for an additional 3-5 minutes in preparation for diquat elution. Note : allowing the column to dry before the methanol wash resulted in reduced recoveries. Final elution was carried out by placing the cartridge, topped with Cartridge Eluent (4.5 mL), inside the top of a 15 mL graduated plastic collection tube and allowing it to drip (flow rate < 1.0 mL / min). The

last bits of eluent were blown into the collection tube with a pipet bulb, 150  $\mu$ L of Ion Pair concentrate were added, the total volume brought up to 5 mL with Cartridge Eluent and the sample vortexed. At this point samples could either be stored under refrigeration or transferred via automatic pipet into polypropylene autosampler vials (0.7 mL) for LC Ion Pair analysis.

Chromatography was carried out using a Hewlett-Packard model 1100 liquid chromatograph equipped with a diode array detector. Diquat was chromatographed on a pair of Hamilton PRP-1 columns (5  $\mu$ m, 4.1 mm x 150 mm) in tandem using the isocratic Mobile Phase previously described at 2.0 mL / min, 30°C. The analyte was monitored at 308 nm (16 nm bandwidth) without background subtraction and emerged at 4.1 min. Injections of 100  $\mu$ L were used.

Quantification was provided by comparison to a 5-point standard curve covering the range from 0.15 to 15 ng/ $\mu$ L of diquat (corresponding to 3 to 300 ppb of diquat in original sample). Standards were injected at the beginning of a sample set and then again after every 10 samples.

*Quality Control* : Along with each sample set (a set being a group of samples collected after the same spray event) were run two laboratory blanks, two blank field water samples, four laboratory spikes and three spiked field water samples.

## RESULTS AND DISCUSSION

### *Linearity of Analysis*

Concentrations of diquat of 0.15, 0.50, 1.50, 50.00, and 150.00 ng/ $\mu$ L (corresponding to 3, 10, 30, 100 and to 300 ppb in the original water sample) were injected into the chromatograph, using an autosampler. All least-squares linear fits generated in the study had correlation coefficients  $\geq$  0.9998. The MDL of 3 ppb is not based on signal-to-noise considerations but on diquat background, which asserted itself soon after the second sample set and proved very difficult to remove.

### *Recoveries of Laboratory and Field water Spikes.*

When all laboratory spikes were taken together the average recovery for the analysis was  $88.41 \pm 8.1$  % (n = 20). When all field water spikes were taken together the average recovery for the analysis was  $76.46 \pm 10.0$  % (n=16). We attribute the difference between these to binding to particulates in the field water. Field blanks averaged out to  $1.3 \pm 1.7$  ppb (n = 11), while lab blanks were  $0.7 \pm 0.8$  ppb (n=10).

### *Diquat Persistence Data*

Tables I to 5 show the levels of diquat obtained over time at White Slough, Owl Harbor, and Sand Mound Slough. Figures 1-5 show the same data in graphical form, with top and bottom values for each site adjacent.

WHITE SLOUGH : 1ST DIQUAT APPLICATION						
		Hours After Application				
	Site #	1	3	6	12	24
<b>Top</b>	1	0.6	2.5	16.0	14.0	3.9
	2	31.1	10.6	31.5	14.4	9.1
	3	5.2	2.7	40.4	7.6	3.1
	4	223.7	28.0	12.0	8.4	4.6
	5	130.8	77.5	7.1	7.2	6.5
<b>Bottom</b>	1	0.6	0.8	28.1	11.4	7.4
	2	0.0	19.7	36.0	11.4	9.8
	3	3.8	4.8	25.1	6.1	0.5
	4	8.5	40.7	14.0	7.7	11.8
	5	144.7	57.1	1.2	6.1	6.6

Table 1 : Persistence of Diquat at White Slough, June 1, 1998. Tank mix was quantified at 191.86 ppm.

OWL HARBOR : 1ST DIQUAT APPLICATION						
		Hours After Application				
	Site #	1	3	6	12	24
<b>Top</b>	1	0.7	104.2	64.3	10.8	4.6
	2	129.1	23.7	52.5	11.6	2.7
	3	134.7	107.1	102.2	39.7	9.4
	4	43.3	6.5	62.5	7.6	5.8
	5	1.8	0.3	19.1	1.5	3.2
<b>Bottom</b>	1	2.0	1.4	4.6	2.5	2.9
	2	151.0	32.9	9.9	1.6	0.6
	3	198.1	164.2	39.2	27.9	12.5
	4	46.7	125.0	3.2	2.4	3.5
	5	2.4	2.3	10.4	4.9	2.2

Table 2 (above) : Persistence of Diquat at Owl Harbor, June 3, 1998. Diquat levels given in ppb.

Table 3 (below): Persistence of Diquat at Owl Harbor, July 22, 1998. Diquat levels listed in ppb. Tank mix was quantified at 178.22 ppm

OWL HARBOR : 2ND DIQUAT APPLICATION						
		Hours After Application				
	Site #	1	3	6	12	24
<b>Top</b>	1	-0.4	129.4	62.0	38.9	4.7
	2	153.4	82.7	108.2	21.9	7.7
	3	329.6	216.2	176.2	64.3	57.0
	4	257.2	127.2	43.9	27.5	7.8
	5	-0.2	106.0	24.0	16.7	10.1
<b>Bottom</b>	1	247.4	1.9	13.8	9.3	0.3
	2	333.4	16.7	44.8	2.0	3.4
	3	359.3	202.8	568.0	223.1	12.2
	4	252.5	1.0	0.9	30.3	6.5
	5	0.4	3.7	4.9	11.0	4.3

SAND MOUND : 1ST DIQUAT APPLICATION						
		Hours After Application				
	Site #	1	3	6	12	24
<b>Top</b>	1	4.7	2.1	16.5	6.0	9.3
	2	1.2	13.9	1.0	0.4	8.1
	3	298.1	65.2	0.8	24.4	1.9
	4	240.0	77.7	1.3	1.2	1.3
	5	197.5	2.2	1.0	9.9	1.5
<b>Bottom</b>	1	4.4	2.4	8.5	11.5	10.1
	2	2.2	1.4	0.8	12.3	4.5
	3	206.6	52.4	27.3	14.7	2.6
	4	181.8	87.5	4.9	5.5	1.4
	5	197.1	207.9	20.4	5.8	1.2

Table 4 (above) : Persistence of Diquat at Sand Mound Slough, June 5, 1998. Diquat levels given in ppb. Tank mix quantified at 235.19 ppm.

Table 5 (below) : Persistence of Diquat at Sand Mound Slough, July 24, 1998. Diquat levels given in ppb.

SAND MOUND : 2ND DIQUAT APPLICATION						
		Hours After Application				
	Site #	1	3	6	12	24
<b>Top</b>	1	6.5	2.4	25.6	17.5	7.1
	2	5.7	22.9	25.5	18.9	9.5
	3	8.0	52.2	12.2	10.3	3.3
	4	178.8	79.7	38.5	16.7	2.3
	5	12.8	56.4	55.9	19.9	0.5
<b>Bottom</b>	1	2.1	117.0	118.6	33.8	0.9
	2	7.6	121.1	107.6	17.6	3.8
	3	5.1	93.2	155.8	14.8	3.3
	4	187.6	62.6	19.7	16.5	1.0
	5	80.2	56.5	6.1	15.6	0.6

At 1 hour after application comparison of top and bottom samples at all sites showed substantial mixing of diquat in the water column. Certain sites were associated with a higher persistence of diquat than others, with Owl Harbor > Sand Mound Slough > White Slough. There were however, differences between individual spray events. Under favorable conditions (OH, 1st and 2nd application, SM, 2nd application) concentrations of diquat at the center of the test plot remained at 30-75 % of initial levels after 3 hours and continued to be significant even after 6 hours. In some cases (SM, OH, 2nd application) the herbicide sank, actually enhancing the diquat bottom levels at 6 hours (Fig 2). Under these conditions diquat provided moderate control of *Egeria densa*.

Under conditions of faster water movement (WS) dissipation was rapid. Off-site movement (to site 5) was major at WS at 1 hour, and diquat was < 45 ppb for the entire test plot at 3 hours. Under these conditions control of diquat was not very efficacious.

As expected, the lifetime of diquat in a tidal environment is shorter than that observed for closed ponds. Many literature studies, designed to represent a “worse case” situation in terms of diquat persistence in the environment, applied diquat at the maximum label rate (1 mg/liter or 1.0 ppm) and followed it over time. Several studies found a level of 10 ppb to be reached at 4 or 5 days (4,6). More rapid dissipation of diquat (< 3 ppb in 36 hours) was found in ponds with dense infestations of algae and macrophytes and high clay particulate content (2).

In our study the nominal levels of diquat applied were lower than in literature (0.25 to 0.37 ppm). Because of tidal movement, which pushes a water parcel in and out of the study area, half-life calculations based on fixed sampling points are not reliable. However, in 4 out of 5 applications the 10 ppb potable water tolerance was reached between 12 and 24 hours.

One influence on the persistence of diquat is the degree to which each area was infested with *Egeria* at the time of application. In the earlier (June) sprayings all three sites had major infestations. In the later (July) sprayings, there was little *Egeria* left. This may account for the observation that diquat sank to the bottom during the second spraying at both Sand Mound and Owl Harbor. The tendency to sink may have been counteracted by adsorption to *Egeria* in the earlier sprayings.

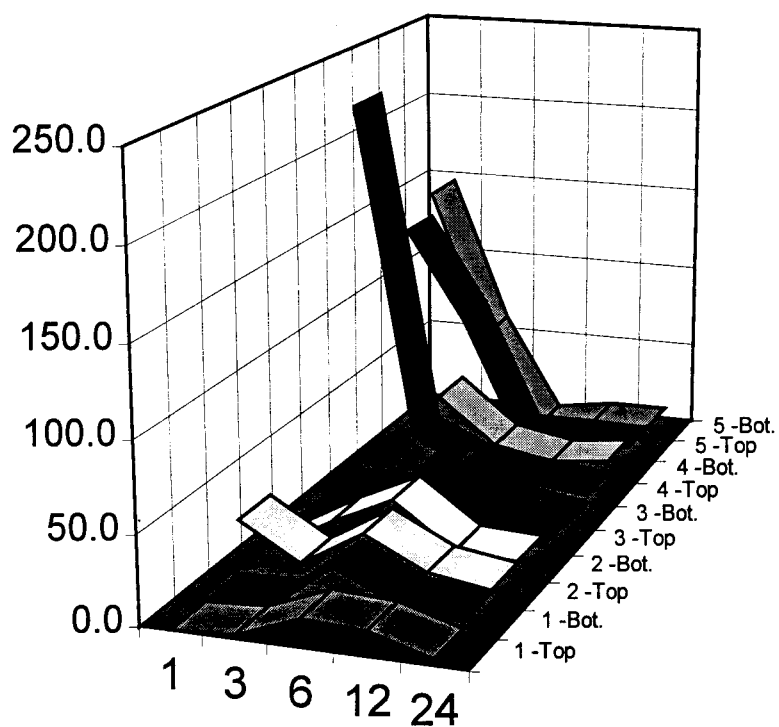
We tried correlating levels of diquat achieved with the point in the tidal cycle the application took place and found that differences in spray events could be partly explained by these influences. Figures 6 to 10 represent the relationship between three quantities: the tide level (in feet above mean lower low tide), the tide velocity (in knots or nautical miles per hour - ebb tides are shown as negative, while flood tides are positive), and the level of diquat (ppb, left scale). The optimal time to apply diquat seems to be 2-3 hours before slack tide on the tide velocity graph, which corresponds with low tide on the tide graph. This was done for Owl Harbor (2nd application), and for Sand Mound Slough (1st application) resulting in initial values of 330 and 300 ppb respectively and longer persistence. This strategy was not followed at White Slough, where application occurred 4 hours before low tide, at a period of maximum tide velocity, resulting in offsite movement of diquat to location 5. Sand Mound Slough (2nd application) also occurred 4 hours before slack/low tide and showed persistence of diquat but lower levels at 1

hour. At Owl Harbor ( 1st application) spray coincided with low tide and tide velocity was rising. There was increased persistence (slack tide occurred 4 hours later, at high tide) but the initial level of diquat achieved was low ( 130ppb vs 330 ppb in application 2). Spraying at the optimal time may help control the variability between individual spray events at the same location, but it must be remembered that many other factors ( density of vegetation, amount of silt, even wind velocity ) affect diquat applications.

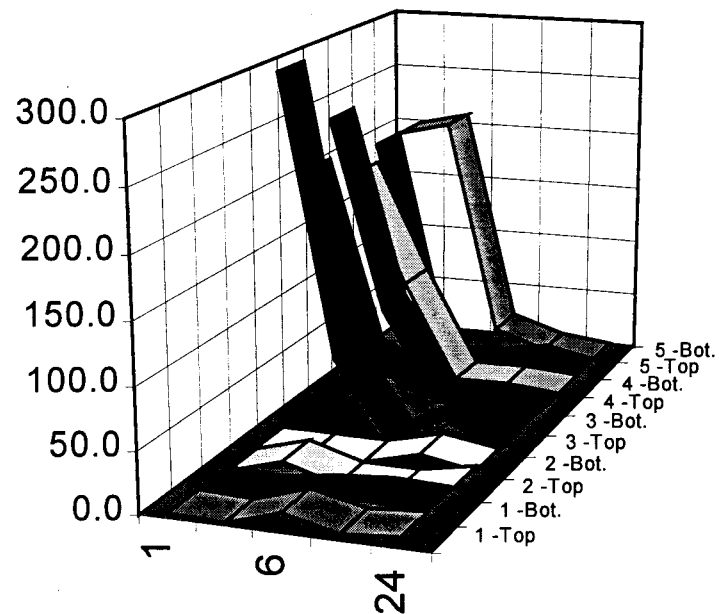
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- (2) "Diquat Distribution In Water After Application to Submersed Weeds", K.A. Langeland, A.M. Fox, F.B Laroche, B.B Martin, D.F. Martin, C.D. Norris, and C. Wang. *Water Resources Bulletin*, Vol 30, # 1 p 93-97 (1994)
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- (6) Herbicidal Residues in Pond Water and Hydrosol, P.A. Frank, and R.D. Comes, *Weeds*, Vol. 15, 210-213. (1967)

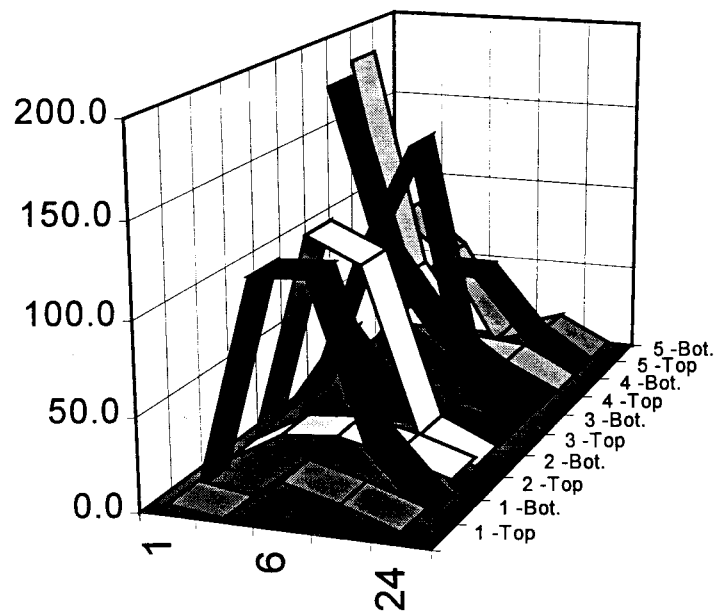
# White Slough: 1st Application



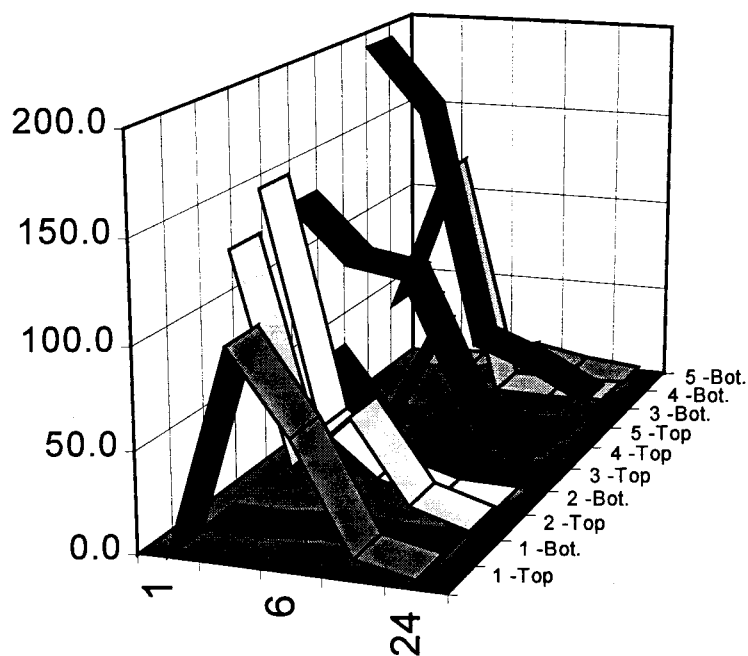
## Sand Mound : 1st Application



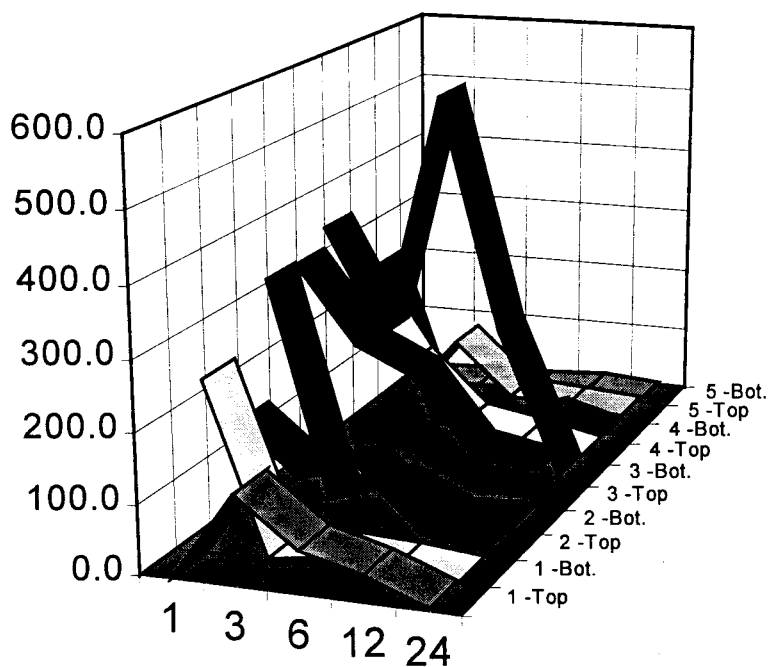
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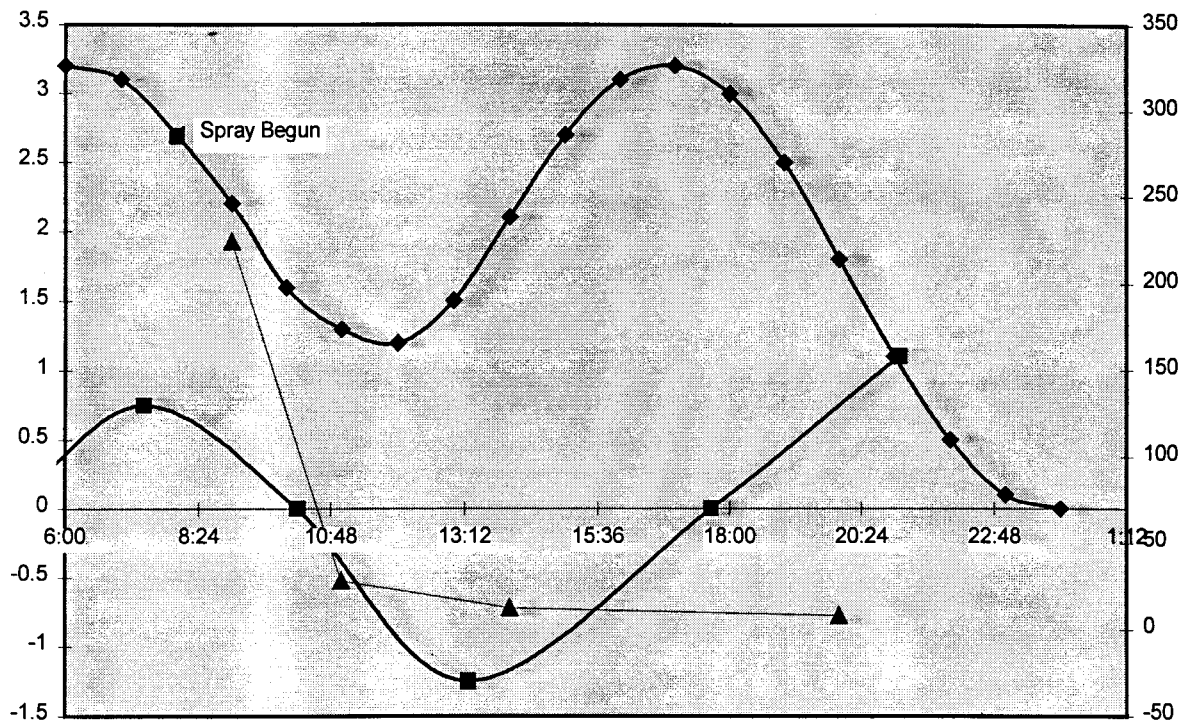
## Owl Harbor: 1st Application



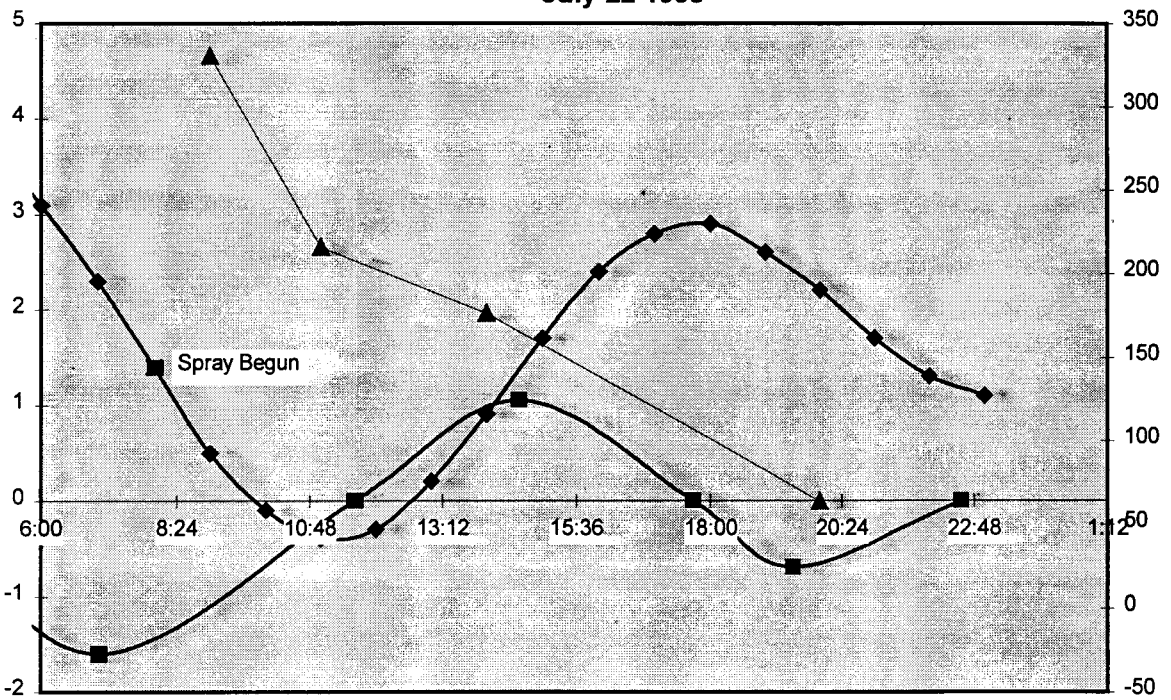
## Owl Harbor: 2nd Application



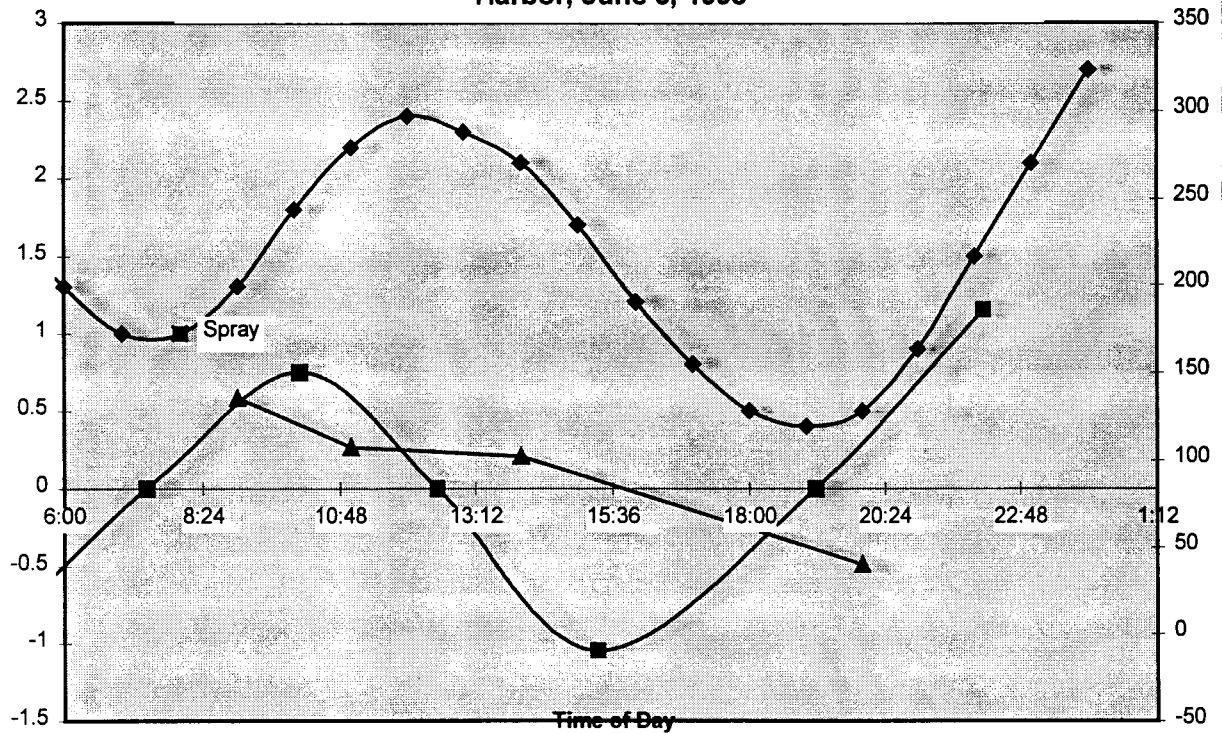
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June 1 1998**



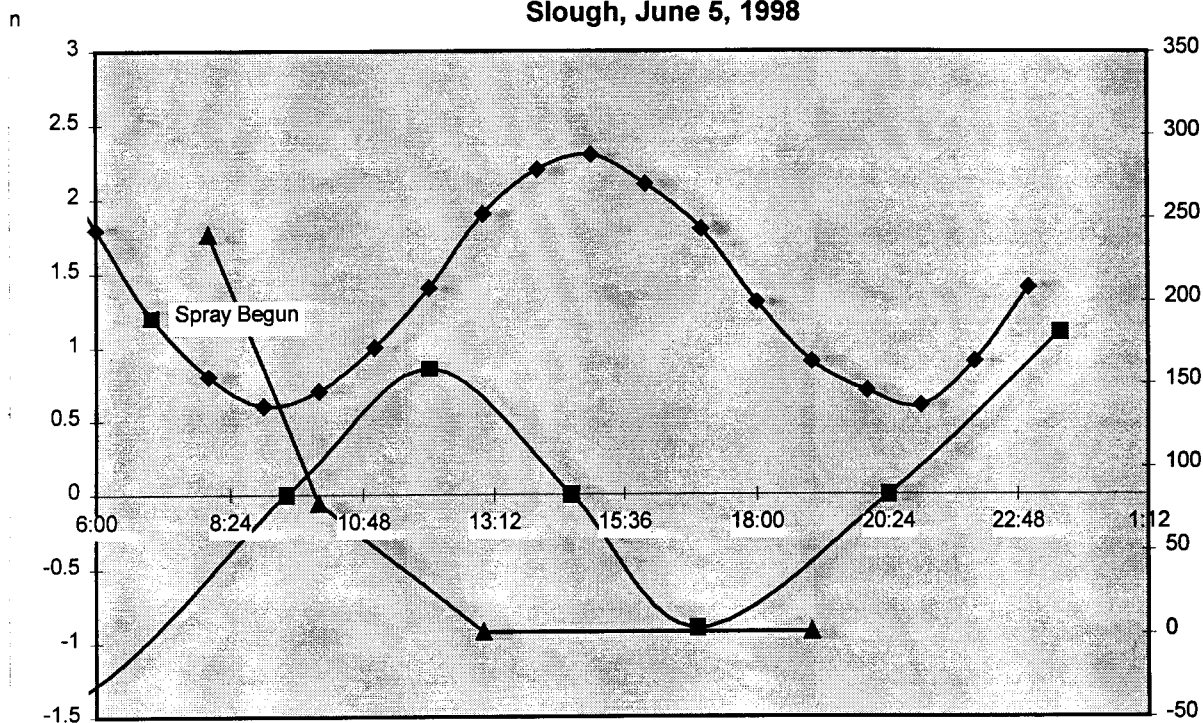
**Relation of Tide Level, Tide Velocity and Diquat Level at Owl Harbor,  
July 22 1998**



**Relation Between Tide Level, Tide Velocity and Diquat Level, Owl  
Harbor, June 3, 1998**



**Relation of Tide Level, Tide Velocity and Diquat Level at Sand Mound Slough, June 5, 1998**



**Relation of Tide Level, Tide Velocity and Diquat Level at Sand Mound Slough, July 24 1998**

